NEW BAND SYSTEMS OF THE TlCl MOLECULE

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Plate XIX

ABSTRACT. The spectrum of thallium chloride is photographed in a high frequency discharge in the first order of a 10 ft. concave grating, having a dispersion of 5.7 Å/mm. Two new systems of bands, one between λ 4300 —λ 4150 designated here as *A*, and the other between λ 4150—λ 3800 designated as *B*, have been obtained in addition to the ultraviolet system around λ 3200 analysed by Howell and Coulson. System *B* consists of about 75 bands in all, which are degraded in either directions while a few of them are headless and diffuse. System *A* consists of about 18 bands which are mostly degraded towards the red, while a few of them are violet-degraded. The vibrational analyses of these two systems have shown that the lower state, which is found to be common to both of them, is the upper state of the ultraviolet system, $^3\Pi - {}^1\Sigma^+$. Predissociation, similar to that found in the upper state of the ultraviolet system, is observed in the lower state of both the systems at $v''=5$. The following vibrational constants have been determined for the two systems.

		$\omega_e' = 101.3$	$\omega'' = 205.5$
System *B*	$\nu_e = 24683.3$	$x_e'\omega_e'' = 0.1$	$x_e''\omega_e'' = 6.5$
System *A*	$\nu_{0,0} \sim 24040$	$\omega_e' \sim 100$,	$\omega_e'' \sim 206$

The chlorine isotope effect observed in some bands in the two systems supports the vibrational analyses.

The close proximity of these two systems suggests that the upper levels may form an electronic doublet.

INTRODUCTION

The early work on this molecule was due to Butkow (1929) who recorded bands in absorption in the region λ 3400—λ 3200 using a dispersion of 17 Å/mm. He measured 49 bands in all and ascribed them to the molecules $TlCl^{35}$ and $TlCl^{37}$. He proposed an analysis of these bands fitted into the following quantum formula :—

$$\nu = 31036.0 - 283.7n'' + 1.10n''^2 + 428.5n' - 202.6n'^2 + 50.6n'^3 - 4.85n'^4.$$

Howell and Coulson (1938) photographed the spectrum of thallium chloride both in emission and absorption on a Hilger E_1 spectrograph having a dispersion of 6 Å/mm. at λ 3200. Excluding isotopic heads and diffuse bands, they measured 59 bands and showed that Butkow's analysis is incorrect. They were able to identify and measure the positions of the band orignis and the following formulae have been derived for the *Q* and *R* heads.

$$\nu_Q = 31054.2 - 287.(v'' + \tfrac{1}{2}) + 1.24(v'' + \tfrac{1}{2})^2 + 216.91(v' + \tfrac{1}{2}) - 6.80(v' + \tfrac{1}{2})^2.$$

$$\nu_R = 31079.6 + 204.0u' - 5.15u'^2 - 284.8u'' + 0.9u''^2.$$

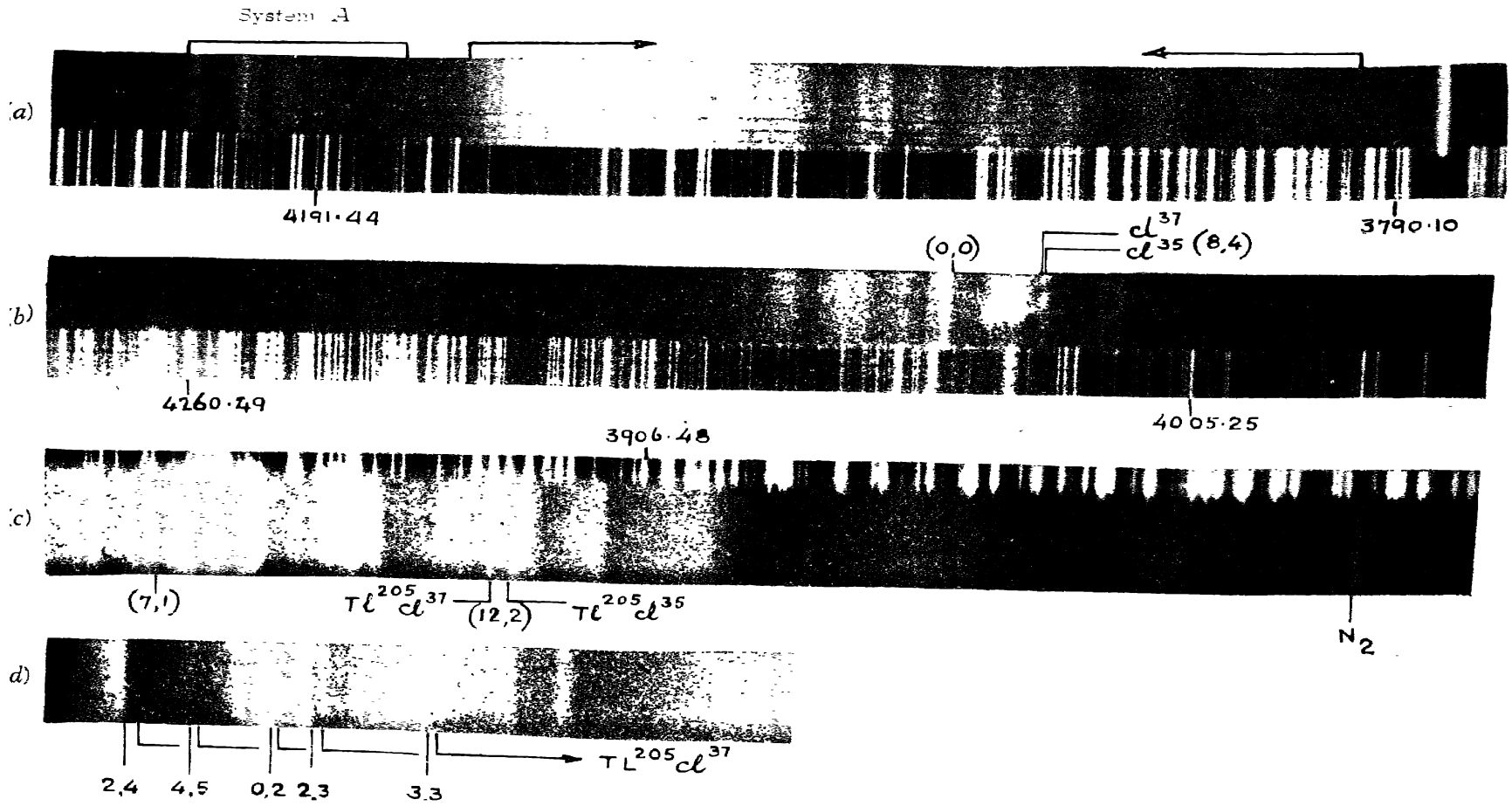
Confirmation of their analysis was obtained by the variation of the $\nu - \nu_0$ interval in the bands in accordance with theoretical expectations and also from the chlorine isotope shifts observed in 38 bands. Neujmin (1934) reported diffuse bands and a continuum in absorption around λ 2510 and measured 13 bands on the red edge of this continuum and 4 on the violet side of the band system analysed by Howell and Coulson. He interpreted them as due to transitions from successive v'' levels to two unstable electronic levels. The existence of these bands in absorption was also confirmed by Howell and Coulson.

In the course of a series of investigations on the molecular spectra of the diatomic halides of thallium, the author photographed the spectrum of thallium chloride in emission in a high frequency discharge. The following results have been obtained: (*a*) the band system between λ 3500—λ3150 analysed by Howell and Coulson, (*b*) a continuum and diffuse bands around λ2500 observed by Neujmin, (*c*) two new systems of bands, one between λ 4150—λ 3800 and the other between λ 4300—λ 4150 not recorded in any previous investigation (See note at the end). The present paper reports the vibrational analysis of these two systems attributed to the TlCl molecule.

The experimental method for developing the emission spectrum of thallium chloride is the same as that for the other halides of thallium and described in detail previously (Rao and Rao, 1949). The spectrum was excited by a low power high frequency oscillator using external electrodes. The discharge was bright green in colour due to the intense λ 5350 Tl line. Intermittent heating at regular intervals was found necessary to maintain the discharge.

The spectrum was photographed on a number of spectrographs. (1) Hilger constant deviation (2) Hilger glass Littrow (8—12 Å/mm. in the region covered by the band systems) (3) Hilger quartz Littrow (11 A/mm. at λ 3900) (4) 10 ft. concave grating with a dispersion of 5.7 A/mm. in the first order. An exposure of 45 minutes was found sufficient with Hilger constant deviation spectrograph using Ilford Selochrome plates. Exposures varying from 1 to 2 hours were given on Ilford special rapid plates while using the other spectrographs.

Measurements were made on the band heads; the type of band origins similar to those observed by Howell and Coulson in the main system are not observed in the new systems. The iron arc lines served as wavelength standards for reducing the plates. The plates taken on all the spectrographs were measured, though band data measured from the grating plates were finally adopted, owing to its high dispersion. About 18 bands in the less refrangible system which may be designated as system *A* and 75 in the other system *B* could be measured in all.



Thallium chloride bands.

(*a*) Quartz Littrow, (*b*) Glass Littrow (*c*) and (*d*) Concave grating spectrograms.

DESCRIPTION OF THE SPECTRUM

Photographs of the spectra illustrating their main features taken on the various instruments are reproduced in Plate XIX in four strips. Strip (*a*) is an overall picture of the two systems of bands in the region λ 4300—λ 3800 taken on the quartz Littrow spectrograph. System *A* consists mostly of bands clearly degraded towards the red, while a few of them are violet-

TABLE I

TlCl bands. System *B*

Wave-length	Int.	Wavenumber	Classi-fication	Wave-length	Int.	Wavenumber	Classi-fication
4124.91	2	24236.1		3981.88 R	2	25106.7	13, 5
21.53 V	2	24256.0	3, 4	77 73 R	3	25132.9	5, 0
19.65 V	4	24267.1	0, 2	76.46 R	3	25140.9	7, 1
15.45	2	24291.9	..	73.37	3	25160.5	9, 2
11.37 V	3	24316.0	5, 5	70 43 R	4	25179.1	..
07.93 R	5	24336.3	...	68.35	3	25192 3	11, 3
04.24 D	2	24358.2	4, 4	61.70	5	25234.6	6, 0
00.66 R	5	24379.5	1, 2	57.87	1	25259.0	10, 2
4096.52 R	6	24404.1		55.38	2	25274.9	...
94.70 R	3	24415.0	3, 3	50.87	2	25303.8	15, 5
92 61 D	2	24427.4	6, 5	47.38	3	25326.1	...
90.47 V	4	24440.2	...	44.41 R	3	25345 2	9, 1
85 30 V	7	24471.1	0, 1	41.65	1	25362.9	11, 2
79.45 R	6	24506.2	2, 2	37.85	0	25387.4	13, 3
68.69 R	4	24571.0	4, 3	35.94	2	25399 7	16, 5
64.32 V	5	24597.4	3, 2	30.22 R	1	25436.7	8, 0
59.31 R	10	24627.8	5, 3	28.45 V	2	25448.2	12, 2
57.03 R	2	24641.6	0, 0	27.01	1	25457.5	...
55.24 R	2	24652.5	2, 1	3925.38 V	5	25468.1	12, 2
52.70	1	24668.0	7, 4	21.16 V	1	25495.5	17, 5
50.48 V	5	24681.5	4, 2	16.55	1	25525.5	...
47.70 V	2	24698.4	6, 3	13.82 V	3	25543.3	9, 0
45.13 V	6	24714.1	9, 5	11.84 R	4	25556.0	13, 2
41.82	2	24734.4	1, 0	10.30 R	2	25566.3	...
39.09	3	24751 1	8, 4	09.05	2	25574 5	15, 3
38 40 V	7	24755.3	8, 4	02.76 V	3	25615.7	...
31.77	2	24796.0	7, 3				
27.69	2	24821.1	10, 5	3898.72 V	3	25642.2	10, 0
				89.74	2	25701.4	19, 5
4024 00 D	5	24843.9	4, 1	86.56 R	3	25722.4	...
20.21 D	5	24867.3	6, 2	83.10 V	4	25745.4	11, 0
15.13 R	4	24898.8	8, 3	79.00 D	2	25770 6	17, 3
08.39 R	3	24940.7	5, 1	73.46 V	2	25809.4	...
05.10	2	24961.1	7, 2	67.49 V	3	25849.3	12, 0
00.71	4	24988.5	...	63.92 R	3	25873.1	...
				61 07 V	3	25892.2	20, 5
3998.16 R	3	24998.2	9, 3	35.99	3	26061.5	20, 3
96.61	1	25014.2	12, 5	32.88	4	26082 7	22, 5
91.75	3	25044.6	6, 1	28.16 R	2	26114.8	21, 4
84.04 R	2	25093.1	10, 3	23.51 V	1	26146.6	15, 0

R indicates that the band is red-degraded
V ,, ,, is violet-degraded
D ,, ,, is diffuse
the degradation of the other bands is uncertain.

degraded. The other system *B* consists of bands degraded either way, though a few of them are diffuse and headless. Bands belonging to this system are very intense between λ 4100—λ 4000 and these are separately shown in strip (*b*) which is an enlargement taken on the glass Littrow instrument. Strip (*c*) is a reproduction of a portion of system *B* between λ 4000—λ 3800 taken on the 10 ft. concave grating. Strip (*d*) is an enlargement of system *A* taken on the grating.

The intensities of the bands are assigned visually on a 0—10 scale.

RESULTS

Table I gives the wavelength, intensity and other data of system *B* and Table II gives the data for the other system *A*. The tables are self-explanatory.

TABLE II

TlCl bands. System *A*

Wave-length	Int.	Wave-number	Classification	Wave-length	Int.	Wave-number	Classification
4244.21 R	3	22554.9	2, 4	4210.29 V	3	23744.7	4, 4
41.97	1	22567.3	$2, 4^1$	04.21 R	2	23779.0	1, 4
34.45	1	23609.2	1, 5	00.50 R	4	23800.0	3, 3
33.04	0	23617.1	$4, 5^1$	4199.18	1	23807.5	$3, 3^1$
27.13 V	2	23650.1	3, 4	94.28	1	23835.3	5, 4
23.31 R	8	23671.5	0, 2	88.45 R	3	23868.5	2, 2
21.8?	3	23679.8	$0, 2^1$	84.75	1	23889.6	4, 3
17.43 R	5	23704.5	2, 3	81.58 V	4	23907.7	7, 5
15.45	2	23715.6	$2, 3^1$	57.65	2	24045.3	3, 1

VIBRATIONAL ANALYSIS OF SYSTEM *B*

The band system presents a complicated appearance owing to the absence of conspicuous sequences or progressions. Though most of the bands are clearly red-degraded, some of them are degraded towards the violet, while others are headless and diffuse but intense. Such a feature is usually observed in the case of band systems for which the vibrational frequencies of the upper and lower states are of the same order of magnitude. But this would mean that discrete close sequences should be noticed, which is not at all a prominent feature of the system. The complicated appearance, then, may be due to overlapping sequences due possibly to fairly large difference between the vibrational frequencies of the upper and lower states. Such relative values of ω'_e and ω''_e should give rise to large chlorine isotopic separations while

most of the bands are not accompanied by the weaker isotope heads. But, this, however, is not a serious difficulty, as the isotopic shifts depend also upon the vibrational quantum numbers of the bands.

As a first step, an attempt is made to pick out progressions with an interval of about 287 cm.$^{-1}$ which is the ground state frequency established from the analysis of the main band system between λ 3500—λ 3150, but this proved futile. The failure to build up the analysis on this basis seemed reasonable as the band system has not been obtained in absorption in any previous investigation. The possibility of analysing the red-degraded bands into one system and the violet-degraded bands into another was also tried but without success. After a number of attempts, it was found that an interval of approximately 100 wavenumber units is found to occur between many bands in the system. A few progressions with this interval could thus be built up which are arranged in a Deslander's scheme. The intervals between the vibrational levels of the lower state of this system are found to be of the same order of magnitude as those of the upper state of the main system. Hence it was considered that the upper state of the main system may be the lower state of the present system. On this basis, the vibrational matrix shown in Table III could be built up to include almost all the bands in the system. The classification of the bands is shown in the last column of Table I. The most intense band in the spectrum is classified as the (0,0) band but the

TABLE III

Vibrational Analysis of TlCl Bands (System *B*)

v' \ v''	0	1	2	3	4	5	6	
0	24627.8	24440.2	24267.1					$\Delta G(v')$
1	24734.4							
2		24641.6	24471.1					
3			24571.0	24404.1	24256.0			
4		24843.9	24668.0	24506.2	24358.2			100.4
5	25132.9	24940.7	24765.7	24597.4		24316.0		97.3
6	25236.6	25044.6	24867.3	24698.4		24415.0		102.1
7		25140.9	24961.1	24796.0	24652.5			95.9
8	25436.7			24898.9	24755.3			100.2
9	25543.3	25345.2	25160.5	24998.2		24714.1		99.3
10	25642.2		25259.0	25093.1		24821.1		97.4
11	25745.4		25362.9	25192.3				
12	25849.3		25468.1			25014.2		
13			25556.0	25387.4		25106.7		
14								
15	26146.6			25574.5		25303.8		
16						25399.7		
17				25770.6		25495.5		
18				25873.1				
19						25701.4		
20				26061.5		25892.2		
21					26114.5			
22						26082.7		
$\Delta G(v'')$	193.2	178.5	166.5	148.1				

TABLE IV

Intensity Distribution in System *B*.

v' \ v''	0	1	2	3	4	5
0	10	4	4			
1	2					
2		2	7			
3			4	6	2	
4		5	1	6	2	
5	3	3	1	5		
6	5	3	5	2		
7	3	3	2	2	2	
8	1			4	7	
9	3	3	3	3		6
10	3		1	2		2
11	4		1	3		
12	3		5			1
13			2	0		2
14						
15	1			2		2
16						2
17				2		1
18				3		
19						2
20				3		3
21					2	
22						4

abnormal intensity of this band may partly be due to the superposition of the (0,3) band at λ 4059.4 of the second positive system of N_2. Some bands in the (v', 0) progression can as well be fitted in the (v', 1) progression since in this region of the table the upper state vibrational level interval is about one-half of that of the lower state. The absence of some bands in the (v', 4) progression is probably due to the overlapping of some of the bands of the (v', 1) progression.

Since band origins similar to those observed in the main system are not observed in the present system, the wavenumber data for the band heads (R or P) only are represented in the scheme. The differences between R—R heads and P—P heads were used in the evaluation of the vibrational constants taking band head data for which accurate measurements have been possible. The ν_e values calculated from bands distributed all over the scheme are found to be fairly consistent. The band heads can be represented by the following quantum formula

$$\nu = 24683.3 + (101.3\ u'. - 0.1\ u'^2) - (206.5\ u'' - 6.5\ u''^2)$$

The following points lend support to the analysis proposed here.

(1) The absence of bands with $v'' > 5$ indicates a clear case of predissociation in the lower state of this system. This gives further justification for identifying this level with the upper state of the main system in which such a predissociation was also noticed by Howell and Coulson at $v'' = 5$. Thus one of

the electronic levels involved in the emission of this band system is one which is well established for this molecule.

(2) The intensity distribution in the system is shown in Table IV. It can be seen that the locus of the strongest bands falls on a typical condon curve which is to be expected with such relative values of ω_e as occur here. The curve is neither a narrow parabola which means that ω_e values are of the same order nor a wdie open parabola in which case ω_e of one state is a small fraction of that of the other.

(3) The isotopic shifts for Tl^{205} Cl^{37} molecule are calculated with the help of the formula

$$\nu_i - \nu = (\rho - 1)\ (\omega_e' u' - \omega_e'' u'') - (\rho^2 - 1)\ (x_e' \omega_e' u'^2 - x_e'' \omega_e'' u''^2)$$

In spite of the large difference between ω_e' and ω_e'', the expected separations in many cases are small, for the relative values of v' and v'' are such that the main term in the above equation becomes small. In such cases, the isotopic heads must have been either unresolved or lost in the degradation of the main bands. However, for bands involving high v' values, the predicted separations are indeed large ; but such bands are either faint or the calculated positions of the isotopic components coincide with neighbouring main bands. The following two favourable bands for which isotopic heads have been observed with certainty, show separations which are in agreement with the predicted values, as shown in Table V.

TABLE V

Band	Calc. isotopic separation	Obs. isotopic separation
8,4	4.2	4.2
12,2	18.4	19.9

VIBRATIONAL ANALYSIS OF SYSTEM *A*

This system occuring between λ 4300-λ 4150 consists mostly of bands degraded towards the red, though a few of them are violet-degraded. A prominent feature which distinguishes this system from the other is the appearance of the chlorine isotopic heads. For about five bands the Tl^{205} Cl^{37} isotopic components could be detected with certainty. The most intense band at $\nu = 23671.5$ cannot be regarded as the (0,0) band, since with such a classification it was not possible to account for the isotope splitting of the order of 8 wavenumber units. A close examination of the system revealed that the prominent bands at λ 4188.45, 4217.43, 4244.21 form an obvious progression. The order of the $\Delta G(v)$ intervals between these bands suggested that the lower state of this system is the same as that of the other system. On this basis, the quantum array shown in Table VI is built up. The classification of the bands is shown in the last column of Table II.

TABLE VI

v'' / v'	1	2	3	4	5
0		23671.3			
		107.5			
1		23779.0*			
		89.5			
2	24045.3	23868.5	23704.5	23554.9	
	176.8	164.0	95.5	149.6 95.2	
3			23800.0	23650.1	
			89.6	149.9 94.6	
4			23889.6	23744.7	23609.4
				144.9 90.6	
5				23835.3	
6					
7					23907.7

* Measurement uncertain

The $\Delta G(v')$ intervals suggest that the upper state frequency of this system is of the same order of magnitude as that of the upper state of system *B*. As the number of bands is less, the vibrational constants cannot justifiably be determined. The following values may, however, be suggested

$\nu_{0,0} \sim 24040\ \text{cm}^{-1}$. $\omega_e' \sim 100$, $\omega_e'' \sim 206$ (same as for system *B*).

Considering that the lower state is common to both the systems and that the upper vibrational constants are approximately equal, the approximate predicted Tl^{205} Cl^{37} isotopic separations may be compared with those observed in 5 bands, as shown in Table VII.

TABLE VII

Band	Approx.-calc. isotopic separation	Obs isotopic separation
0,2	9.1	8.3
2,3	7.4	11.1
2,4	10.0	12.4
3,3	5.0	7.5
4,5	7.1	7.9

This table shows that the observed separations are of the same order as the predicted values calculated from approximate values of vibrational constants.

The absence of bands with $v'' > 5$ is noteworthy, which indicates a clear case of predissociation in the lower state of this system. This is a further justification for the identification of this level with the lower state of the other system. It is probable that there is predissociation in the upper state also as the number of v' levels observed is limited. This explains why a few bands alone are observed in the system. The intensity distribution in the

bands is shown in Table VIII. As the separation of the (0,0) bands of these two systems is approximately 580 cm^{-1}, it is very probable that the upper levels may form an electronic doublet.

TABLE VIII

	0	1	2	3	4	5
0			8			
1			2			
2		1	3	5	3	
3				4	2	
4				1	3	1
5					1	
6						
7						

ELECTRONIC TRANSITIONS IN TlCl

The electronic states of the related group III elements Al, Ga, In, etc. have been discussed by Miescher and Wehrli (1934 & 1935), Howell and others. Holst (1934) and Jennergren (1948) have established the ground states of the molecules AlCl and AlBr as $^1\Sigma^+$. By analogy, the other molecules may in all probability be a similar $^1\Sigma^+$. Miescher and Wehrli consider that the doublet systems observed in the Ga and In halide spectra are due to forbidden transitions between the ground level and certain components of a triplet level. Both of these systems have a common lower state $^1\Sigma^+$ arising from the electron configuration $\sigma^2\pi^4$. The excitation of one of the π electrons produces the configuration $\sigma^2\pi^3\sigma$ giving rise to the molecular states $^1\Pi$, $^3\Pi_0^+$, $^3\Pi_0^-$, $^3\Pi$, and $^3\Pi_2$ (inverted) Howell suggested that the doublet system in TlF may be identified as due to a forbidden transition $^3\Pi_0$—$^1\Sigma^+$ and $^3\Pi_1$—$^1\Sigma^+$, and the singlet system occurring on the violet side as due to the transition $^1\Pi$—$^1\Sigma^+$. In TlCl, Howell and Coulson found only one component of the doublet system which was identified as due to the transition $^3\Pi_1$—$^1\Sigma^+$. They also suggested that the diffuse bands and continuum in TlCl around λ 2500 may be due to the transition $^1\Pi$—$^1\Sigma^+$. The vibrational analysis of the two new systems analysed in the present work have shown that the lower state of these two systems is the upper state of the system $^3{}_1\Pi$—$^1\Sigma^+$. Hence the lower state of the two systems is a $^3\Pi_1$. To identify the upper states, it is necessary to examine the next higher states resulting from the configuration $\sigma^2\pi^3\pi$. This configuration will give rise to states $^3\Sigma^+$, $^1\Sigma^+$, $^1\Sigma^-$, $^1\Delta$, $^3\Sigma^-$ and $^3\Delta$. The close proximity of the two systems suggests that the upper states may

form an electronic doublet. Hence the upper states are to be identified as two members of a triplet level. Since the lower state is a $^3\Pi_1$, the upper states may be the members of either $^3\Delta$ or a $^3\Pi$ term. Since the doublet separation is only of the order of 580 cm.$^{-1}$ it appears more probable that the upper states may be two members of a $^3\Delta$ term, which is one of the excited states of the electron configuration $\sigma^2\pi^3\pi$.

The author has recently received from Prof. E. Miescher (1941) the reprint of his paper on band spectrum of thallium chloride, in which he recorded some of the bands in both the systems reported here, but no analysis was presented for these bands.

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